
Evaluation of Two Sorbents for the Sorption-Enhanced Methanation in a Dual Fluidized Bed System

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Abstract

The unceasing concern for climate change, closely related to the exploitation of fossil fuels, pushes the scientific community to develop new technologies for CO₂ capture and utilization (CCU). Moreover, the growth and diffusion of solar energy requires new energy storage systems that put solar fuels at the forefront. Methane seems to be a suitable energy vector, which could both store solar energy and exploit fossil fuel derived CO₂. Moreover, methane has the main advantage of an already existing distribution and storage infrastructure.

The methanation reaction from hydrogen and carbon dioxide (or monoxide) is generally carried out in staged adiabatic catalytic fixed beds operated at high pressure in order to overcome thermodynamic limitations. A recently proposed alternative pathway is the sorption-enhanced methanation concept, which is based on the employment of a sorbent able to capture *in situ* the H₂O produced during reaction, to shift equilibrium towards the formation of CH₄.

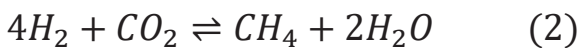
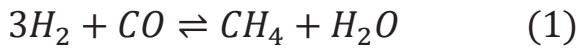
In this work a CaO, derived from natural limestone, and a commercial 3A Zeolite were tested as sorbent materials for H₂O capture in a new configuration for the sorption-enhanced methanation based on the concept of chemical looping in dual interconnected fluidized bed systems. The experimental campaign was aimed at studying the sorbent performance in terms of hydration and dehydration at different operating conditions relevant for catalytic methanation. The results showed that CaO has a good capacity to capture and release steam in the temperature range of interest. Unfortunately, even at the lowest temperatures tested, the sorbent is affected by the presence of CO₂, which worsens its performance in terms of H₂O capture capacity. The zeolite has a more stable behavior than CaO under all investigated conditions. Comparing the performance of the two materials, the zeolite on average has better capture capacity (0.017-0.049 g/g) than CaO (0.006-0.025 g/g) and it is not affected by deactivation during the cycles.

1. Introduction:

Methane is an important energy carrier for many sectors, which features a well-developed distribution and storage infrastructure in many countries, and its massive utilization in the automotive, household and industrial sectors.

Nowadays, natural gas is the main source of methane, however the increasing dispute on global warming related to the exploitation of fossil fuels has moved the interest to alternative and renewable technologies for methane production, such as catalytic and biological methanation processes [1-3].

Specifically, catalytic methanation [4], via CO (Eq.1) or via CO₂ (Eq.2), has several features that makes it very interesting if combined with the concepts of solar fuels, chemical storage and CO₂ utilization. Indeed, methane could act as chemical storage carrier of solar energy [2] initially used to convert water into hydrogen by electrolysis [5]. Moreover, CO₂ methanation could be considered as a process for CO₂ utilization in the framework of Carbon Capture and Utilization (CCU) technologies [6-10]. On the other hand, the production of methane from CO could represent the final step after coal or biomass gasification into syngas [11-13].



The typical catalysts able to promote methanation are based on different metals such as Ru, Ni, Co, Fe, and Mo [14], though Ni-based catalysts are considered to provide the best compromise among activity, selectivity and low price [15-17]. Commercial methanators consist of fixed beds, typically operated at high pressure to obtain high methane yields, and arranged in series in order to carry out intermediate cooling steps and recycles to manage the temperature of the process (due to the high exothermicity of the reaction) [1,20]. In particular, the temperature management represents the main issue for the process because it may lead to the deactivation of the catalyst [18]. In addition, the high temperature can promote carbon deposition on the catalyst surface due to the Boudouard reaction [19]. In the last years, many research groups have proposed new solutions, based on new reactor designs (fluidized bed reactors, three-phase reactors), to improve the current methanation process with the goal to have a better temperature control [2].

Recently, Borgschulte et al. [21] and Walspurger et al. [22] investigated the possibility to enhance the methane production by the application of the concept of Sorption-Enhanced Methanation (SEM), where the steam, produced by the methanation reaction, is continuously removed from the reaction environment by means of a suitable regenerable sorbent material, e.g. a zeolite. These studies demonstrated in a lab scale fixed bed apparatus that the SEM process has the potential for high-grade methane production at low pressure using commercial materials, with the consequence of a relevant energy saving for the entire process.

Based on these promising outcomes, in this work an innovative configuration for the SEM process is proposed. This configuration takes advantage of the chemical looping concept where in one reactor (methanator) catalytic methanation occurs simultaneously with the hydration of a suitable sorbent, so as to drive the equilibrium towards product formation, while the regeneration of the sorbent takes place in another reactor (dehydrator). The two reactors are connected each other in a dual-interconnected fluidized beds configuration as shown in Fig. 1. This scheme has the advantage of a steady operation of the plant, thus avoiding the unsteady cyclic operation necessary for sorbent regeneration in fixed bed reactors. In addition, the use of fluidized bed reactors appears to be suitable to achieve good temperature control for highly exothermic reactions like methanation.

In this work, two potential sorbents were tested for their steam capture potential in a lab-scale dual bed fluidized bed apparatus: CaO, derived from natural limestone, and a commercial 3A-zeolite. The main aim was to evaluate the sorbent performance in terms of hydration and dehydration cycles at different operating conditions relevant for catalytic methanation.

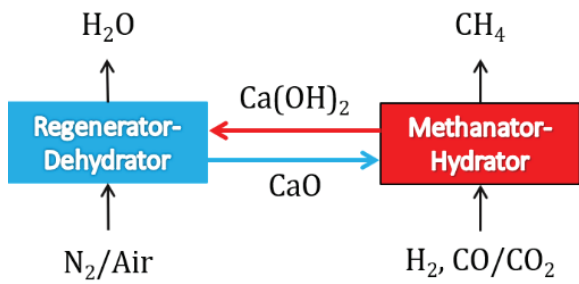


Fig.1: Scheme of the Chemical Looping Sorption-Enhanced Methanation concept

2. Experimental:

Two materials were tested as sorbents for SEM: a CaO and a zeolite. CaO was obtained by calcination of an Italian limestone named Massicci: the material was prepared in a lab-scale fluidized bed at 850°C with air for 20min. The zeolite was a spherical commercial 3A-zeolite.

The experimental apparatus used for the tests, called Twin Beds (Fig.2), consists of two identical lab-scale bubbling fluidized beds connected by a rapid solid transfer line. This system is an ad hoc device used to study looping processes. The two reactors have an inner diameter of 40 mm, and are divided in two sections: a wind box also used as gas preheater; a fluidized bed, separated from the wind box by a perforated plate gas distributor. Both reactors operate separately in batch mode but they are connected each other by a duct (ID 10 mm), partially immersed in both beds, used for fast pneumatic conveying of the sorbent between the two reactors. Transfer of sorbent is accomplished by using a valve system arranged along the duct and at the outlet of the reactors. The solid is injected into the system by a steel hopper connected sideways to the reactor. The apparatus is also equipped with an additional vertical duct, located in the middle between the two beds and connected with the transport duct by means of a 3-way valve; at the bottom of this duct a removable stainless-steel container is placed. The aim of this duct is

to allow a fast discharge of the reactors and to collect the whole bed material into the container at the end of each test. A thorough description of the operating principle of the TB system is reported elsewhere [23].

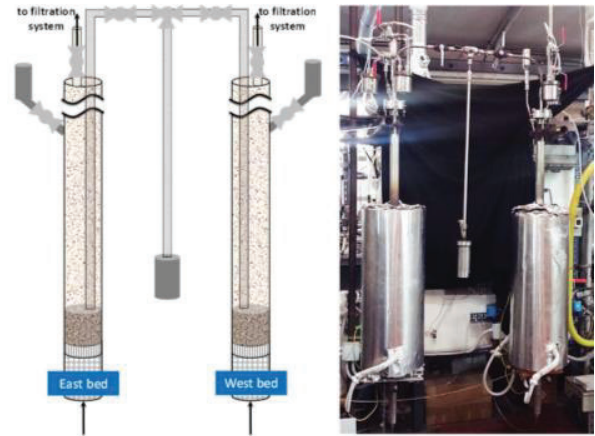


Fig.2: Twin Beds Apparatus

The two reactors were employed as hydrator and dehydrator respectively. The experimental campaign was aimed at evaluating the suitability of the sorbents to capture and release water at different temperatures and reaction environments relevant for methanation. A steam generation system, that permits to produce steam at 200°C, was used to generate the gaseous flow for the hydration step.

The main operating conditions were: hydration with 10% steam (balance air) and dehydration in air. A sensitivity analysis on temperature was carried out varying both the hydration and the dehydration temperature (one at a time, while keeping the other fixed). The temperature range investigated for hydration was 200-300°C, while that for dehydration was 350-450°C. As an example, the acronym M-H25A-D35N is a typical name used to identify one test where the first letter specifies the sorbent (M=Massicci lime; Z=zeolite), H25A indicates the hydration step at 250°C in air, while D35A indicates the dehydration step at 350°C in air. All the conditions investigated are summarized in Table 1.

	Temperature	Fluidizing gas		
		H ₂ O	CO ₂	Balance
X [*] -H20A-D35A	250/350 (°C)**	10/0 (%vol)	400/400 (ppm)	Air/Air
X-H25A-D35A	250/350 (°C)			
X-H25A-D40A	250/400 (°C)			
X-H25A-D45A	250/450 (°C)			
X-H30A-D35A	300/350 (°C)			
X-H30A-D40A	300/400 (°C)			
X-H30A-D45A	300/450 (°C)			

*X=M for Massicci sorbent, =Z for zeolite sorbent

**the first value (250) refers to the hydration stage, the second one (350) to the dehydration stage

Tab.1: Main operating conditions

The progress of hydration and dehydration reactions was followed during the tests by measuring the steam concentration at the outlet of the reactors by means of a calibrated humidity sensor. Each test consisted of 10 complete cycles, with a fluidization velocity fixed at 0.5m/s, while the time of each hydration or dehydration step was fixed at 10 min. The H₂O capture capacity of the material, during each hydration stage, was evaluated by time-integration of the outlet H₂O profile.

3. Results and discussion

Steam capture tests for Massicci CaO.

Figure 3 reports the steam capture capacity of the sorbent with the number of cycles, expressed as grams of captured H₂O per gram of initial CaO, for all the conditions investigated. In general, the performance of CaO tends to decay with the number of cycles, and to reach an asymptotic value after the 6th-7th cycle. Moreover, the 2nd cycle typically presents a higher value of steam capture than the 1st cycle. This trend is most likely due to the different value of molar density between calcium hydroxide and calcium oxide (which is lower for the first one), with a consequent swelling of the particle during the 1st hydration, which entails an alteration of the sorbent microstructure with the formation of a highly porous CaO after the 1st dehydration step [24].

The decay after the 2nd cycle is the consequence of two effects: the first one is the occurrence of attrition phenomena which imply the removal of sorbent

material leaving as fines from the reactor with the outlet gas; the second effect is caused the irreversible carbonation of the CaO with the CO₂ contained in air, consuming active CaO from the sorbent.

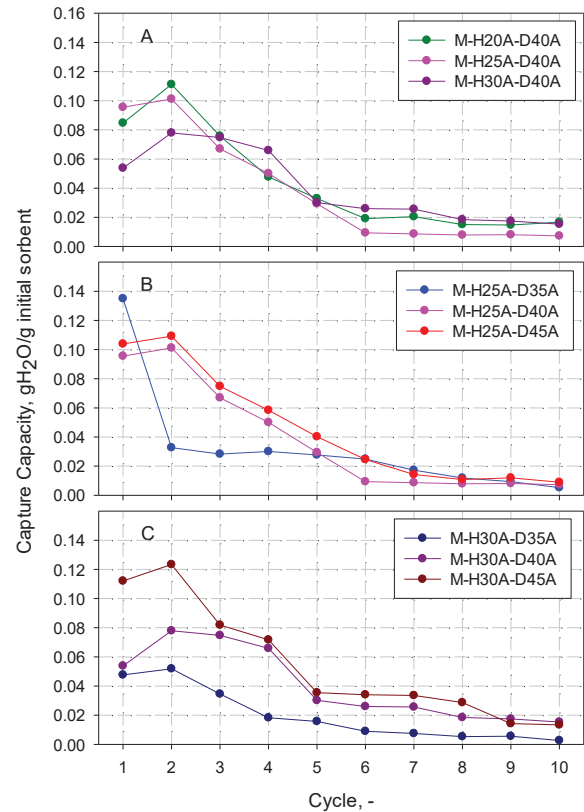


Fig.3: H₂O capture capacity of the sorbent with the number of cycles for Massicci CaO

In Fig. 3-A the results of the tests M-H20A-D40A, M-H25A-D40A and M-H30A-D40A are reported, at a fixed dehydration temperature of 400°C, and for three different hydration temperatures (200, 250 and 300°C). The steam capture capacity decreases with the hydration temperature and this difference is evident during the first cycles and tends to vanish with the increase of the number of cycles. This behavior is related to the higher hydration (and carbonation) kinetics which determines the formation of a plugging layer of Ca(OH)₂ (and CaCO₃) which hinders the diffusion of steam in the particle core. The asymptotic capacity values are similar among the samples and range around 0.008-0.019 g/g.

The effect of the dehydration temperature was investigated setting two different hydration temperatures of 250 and 300°C and varying the dehydration temperature (350, 400 and 450°C). The results are shown in Figs. 3-B and 3-C. In general, the increase of the regeneration (dehydration) temperature improves the steam capture capacity but these differences are only significant during the first cycles and tend to disappear with the increase of the cycle number. Probably, this behavior may be explained by the fact that faster dehydration (at higher temperatures) determines overpressures inside particle that induce a more severe breakage of the particles with the formation of new surface for the subsequent hydration step [25]. However, these effects appear to be more relevant at the highest hydration temperature, in particular during the first cycles (compare Figs. 3-B and 3-C).

Steam capture tests for 3A Zeolite.

Figure 4 (A-C) reports the steam capture capacity of the sorbent with the number of cycles, expressed as grams of captured H₂O per gram of initial zeolite, for all the condition investigated. In general, the behavior of the zeolite is quite stable along the cycles with a slight increase of the capture capacity during the first cycles that indicates a sort of feeble activation.

Similar to CaO, the influence of the hydration temperature was studied fixing the dehydration temperature at 400°C and varying the hydration temperature at 200, 250 and 300°C (Fig. 4-A). It is possible to note a slight negative influence of hydration temperature, in particular for the test Z-H30A-D40A, which shows an average capture value of about 0.022 g/g, compared to 0.044 and 0.049 g/g for Z-H20A-D400A and Z-H25A-D40A, respectively. This effect is due to the worsening of physical absorption of H₂O on the sorbent surface at higher temperatures.

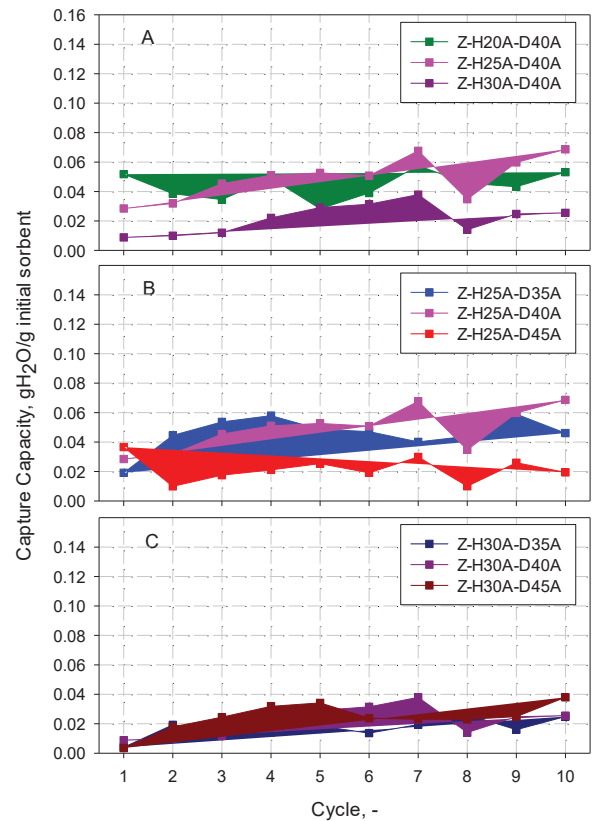


Fig.4: H₂O capture capacity of the sorbent with the number of cycles for 3A Zeolite

In Figs. 4-B and 4-C the effect of the dehydration temperature was examined (350, 400 and 450°C) for two different hydration temperatures (250 and 300°C). In particular, when the hydration temperature was set to 250°C (Fig. 4-B), the increase of the dehydration temperature seems to have a limited effect until 400°C (average values of 0.046 and 0.049 g/g for Z-H25A-D35A and Z-H25A-D40A respectively), while the capture capacity significantly decreases at 450°C (average value of 0.22 g/g for Z-H25A-D45A). This behavior is most likely caused by the chemical degradation of the sorbent at 450°C, probably related to the release of water contained in the zeolite structure.

When the hydration temperature was 300°C, the steam capture capacity records a relevant decay for all investigated dehydration temperatures. As matter of fact, the average capacity values were 0.017, 0.022 and 0.024 g/g for the tests Z-

H30A-D35A, H30A-D40A and H30A-D45A, respectively. Probably, the hydration temperature limits from a thermodynamic point of view the physisorption of water as detected for the tests at different hydration temperatures (see figure 4-A), and this effect is more pronounced when the difference between hydration temperature and dehydration decreases.

4. Conclusions

In this work, the feasibility of two different materials was investigated for their utilization as H₂O sorbents for the Sorption-Enhanced Methanation in an innovative configuration consisting of two interconnected fluidized beds. A calcium oxide, derived from an Italian natural limestone called Massicci, and a commercial 3A zeolite were tested in a lab-scale dual fluidized bed apparatus, called Twin Beds, purposely designed for looping systems. The performance was evaluated in terms of the steam capture capacity and its release in multiple cycle tests of hydration and dehydration. The hydration steps were run in a reaction environment composed by 10% in volume of steam in air, while the dehydration steps in pure air. A sensitivity analysis was carried out at different temperatures of both hydration and dehydration to investigate the effect of these temperatures on both materials.

In general, CaO presents a decay of the steam capture capacity with the number of cycles in all conditions investigated. This decay is likely determined by the combination of chemical deactivation, induced by the irreversible carbonation of the sorbent with CO₂ contained in the air, and the elutriation of fines particles due to attrition phenomena. The increase of the hydration temperature entails a negative effect during the first cycles, which tends to vanish with the increase of the cycle

number. This behavior is probably due to the formation of a plugging external layer of Ca(OH)₂ (and CaCO₃) induced by faster reactions. Conversely, higher dehydration temperatures promote particle breakage with the formation of new surface with the consequent increase of the steam capture capacity.

On the other hand, the zeolite has a more stable behavior than CaO in all conditions investigated, and presents a slight activation during the first cycles. However, the hydration temperature has a similar effect as for CaO, which determines a decrease of the steam capture capacity. The explanation of this trend is due to the less favorable physisorption with the increasing temperature.

Contrary to CaO, the influence of the dehydration temperature on the zeolite seems to be strictly related to the hydration temperature. At low hydration temperature, a negative effect could be observed only at the highest dehydration temperature, probably induced by a modification of the structure of the zeolite. Instead, at higher hydration temperature the steam capture is principally limited by the thermodynamics of physisorption during the hydration stage.

Comparing the performance of the two materials, the zeolite on average has a better asymptotic capture capacity (0.017-0.049 g/g) than CaO (0.006-0.025 g/g) and furthermore it is not affected by deactivation during the cycles. However, this is not the only parameter to be considered for the choice of the best sorbent for the sorption-enhanced methanation, because other features could be important, such as the different cost of the two sorbent, which is in favor of CaO. In addition, another important factor is the attrition resistance of the sorbent in a fluidized bed environment, which will be the subject of future experimental tests. For steady operation in a dual fluidized bed reactor methanator (with continuous

circulation of the sorbent to/from a regenerator reactor), the amount of water removed from the methanation reactor can be regulated by changing the sorbent circulation rate to/from the regenerator or by changing the ratio of sorbent to catalyst loading in the system. It is worth noting that a recent thermodynamic assessment showed that partial water capture might be

preferable with respect to total water removal in order to avoid solid carbon formation (which would lead to catalyst deactivation) [26]. A detailed calculation of the optimal sorbent/catalyst ratio and solids circulation rate would need a preliminary definition of the best operating conditions in terms of the desired fractional amount of captured water.

5. Acknowledgements

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